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RESEARCHES ON MODERN BRISANT NITRO EXPLOSIVES  
By C. F. VAN DUIN AND B. C. ROETERS VAN LENNEP

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RESEARCHES ON MODERN BRISANT NITRO  
EXPLOSIVES\*

BY C. F. VAN DUIN AND B. C. ROETERS VAN LENNEP

Translated by CHARLES E. MUNROE

Chairman, Committee on Explosives Investigations, Division of Chemistry and Chemical Technology, National Research Council

INTRODUCTION

In the examination of explosives there are actually established the following constants according to the methods developed by Bichel,<sup>1</sup> Kast,<sup>2</sup> Will, Dautriche, Noble, etc., and to the principles enunciated by Berthelot,<sup>3</sup> Sarrau, Vieille, Abel and others:

1. Velocity or rate of explosion
2. Energy liberated by the explosion
3. Composition of the products formed
4. Calculated temperature produced by the explosion
5. Pressure in a 15 l. Bichel<sup>4</sup> bomb
6. Enlargement of the cavity in a Trauzl lead block
7. Duration and length of the flame produced by the explosion of 100 g. of the substance
8. Stability and the initiating explosion temperature
9. Sensibility to shock

The greatest weight ought undoubtedly to be assigned to the constants 1, 2, 3, 8 and 9; but as we have not had at our disposal the necessary devices with which to measure the first three, we have

\* From *Recueil des Travaux Chimiques des Pays-Bas*, vol. 39, no. 2, pp. 145-177, Feb. 15, 1920.

<sup>1</sup> Bichel, "Methoden und Apparate der Sprengstoff A. G. Carbonit, zur Prüfung von Sprengstoffen."

<sup>2</sup> Kast, "Anleitung zur chemischen und physikalischen Untersuchung der Spreng- und Zündstoffe," Braunschweig, 1909.

<sup>3</sup> Berthelot, "Sur la force des matières explosives d'après la thermochimie," Paris, 1883.

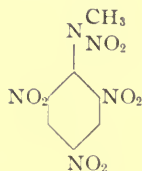
<sup>4</sup> Bichel, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, 3, 365 (1901).

been limited to the determination of the stability and of the sensitiveness to shocks. The two last properties have had a special significance since Flürscheim<sup>1</sup> introduced into the technique of explosives substances having very mobile nitro groups, such as tetranitroaniline, while others have sought to employ the dinitramines.<sup>2</sup>

To render the researches on strongly nitrated compounds having one or more methylnitroamino groups or very mobile nitro groups as complete as possible, we have also sought to derive from the tetranitrophenylmethylnitramine, 2,4,6,2',3',4'-hexanitrodiphenylamine and tetranitrophenol some of those bodies which have not been employed as explosives because of their mode of preparation or their properties.

## PREPARATION AND PROPERTIES

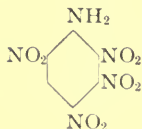
### I. Tetranitrophenylmethylnitramine (Tetryl)



On the subject of this explosive one should consult existing works.<sup>3</sup>

### II. 2,3,4,6-Tetranitroaniline

To the communications which we have already made<sup>4</sup> on the subject of the preparation and the properties of this compound, we now add the results of the study of the action of moist acetone upon it, in which we have identified the products formed in this reaction. By the action of moist acetone on the tetranitroaniline



there are formed large quantities of hydrogen cyanide, together with the trinitroamidophenol previously mentioned. By distillation in a vacuum on the water bath, after having eliminated the acetone, there is obtained an acid liquid, which after neutralization with ammonia is colored black on warming after the addition of a silver salt.<sup>5</sup> We expected to find formic acid present, but have

<sup>1</sup> D. R. P. 241,697 and 243,079.

<sup>2</sup> Brevet français, 391,107.

<sup>3</sup> Van Duin, *Rec. trav. chim.*, **37**, 111 (1917).

<sup>4</sup> Van Duin, *loc. cit.*, 114.

<sup>5</sup> This distillation ought to be conducted with great care, for there remains in the flask very impure trinitroamidophenol, which can give rise to an explosion. See the experience of Van Romburgh on the trinitromethylnitraminophenol. Van Romburgh, *Versl. Kon. Akad. van Wetensch. Amsterdam*, **23**, 1340 (1915).

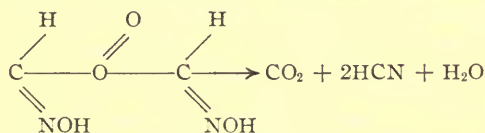
been unable to identify it in the products of the reaction. Apart from the water, which is a most important fraction, the distilled liquid appears to be composed as follows:

a. Formaldehyde.—This can be shown by a direct reduction of a solution of ammoniacal silver oxide and also of a dilute solution of potassium permanganate. It produced also an intense red color, characteristic of formaldehyde, when the liquid was mixed with a solution of 0.1 g. of morphine hydrochloride in 5 cc. of concentrated sulphuric acid.<sup>1</sup>

b. Acetic acid.—After neutralization with soda the liquid was evaporated and the salt obtained identified as sodium acetate, as follows: ferric chloride produced a red color and on boiling there was formed a precipitate of basic ferric acetate. On heating with alcohol and some drops of concentrated sulphuric acid, the odor of ethyl acetate was immediately perceived. On heating with a solution of *p*-nitrobenzyl bromide in 63% alcohol as indicated by Emmet Reid,<sup>2</sup> crystals were obtained which fused at 78°; when these were mixed with *p*-nitrobenzyl acetate, prepared according to the method described by the same author, there was no lowering of the melting point.

It was possible to show the presence of oxalic acid in the residue remaining in the flask. For this purpose the residue was extracted with hot water, neutralized by ammonia, and then acidified by acetic acid. On addition of a solution of calcium chloride there was observed the formation of a precipitate which immediately, when warm, reduced the solution of permanganate of potash slightly acidified by sulphuric acid. Thus products formed in the decomposition of aqueous solutions of di-isonitroso and isonitroso acetone were indicated, though we were not able to isolate them.

It is already known that when an aqueous solution of di-isonitroso acetone is heated, it decomposes as follows:



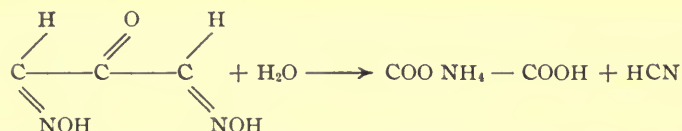
At the same time there is produced a little ammonia, hydrogen cyanide and oxalic acid:<sup>3</sup>

<sup>1</sup> Tendler and Manninck, *Zeitsch. f. anal. Chem.*, **48**, 310 (1909).

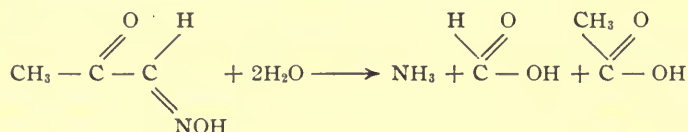
<sup>2</sup> Emmet Reid, *Journ. Amer. Chem. Soc.*, **39**, 124 (1917).

<sup>3</sup> Von Pechmann and Wehsarg, *Ber. d. deutsch. chem. Ges.*, **21**, 2989 (1888).

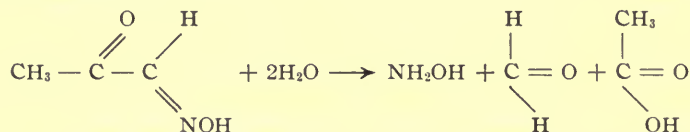




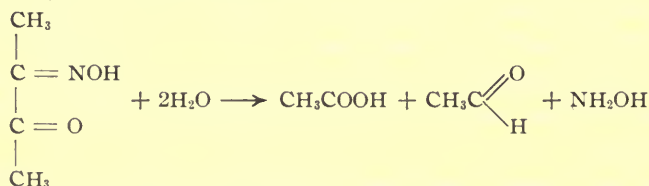
For the isonitroso acetone we have found that when this body is heated to  $140^\circ$  in the presence of dilute hydrochloric acid, it decomposes as follows:<sup>1</sup>



However, given the low temperature at which the action of moist acetone on tetranitroaniline occurs, the reaction can be accurately represented as follows:



This is why it appears, in accordance with the facts cited above, that the acid reaction of the distillate obtained by Van Romburgh, through the action of moist methyl ethyl ketone on tetranitrophenylmethyl nitramine, should be attributed to the presence of acetic acid, and its reducing property to the presence of acetaldehyde. These compounds then appear to be produced from isonitrosomethylethylketone, as follows:



It may be considered established that Flürscheim was the first to knowingly prepare the tetranitroaniline. However, we believe that Witt and Witte<sup>2</sup> have had this substance in hand and have considered it as a trinitroaniline. These authors state that they obtained the 3,4-dinitroacetanilide,<sup>3</sup> melting point  $144^\circ$ , when a

<sup>1</sup> Treadwell and Steiger, *Ber. d. deutsch. chem. Ges.*, **15**, 1059 (1882).

<sup>2</sup> Witt and Witte, *Ibid.*, **41**, 3095 (1908); see also Flürscheim, D. R. P. 243,079.

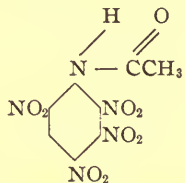
<sup>3</sup> Wender, *Gaz. chim. ital.*, **19**, 225 (1889).

solution of 10 parts of *m*-nitroacetanilide in 100 of 100% sulphuric acid was mixed below  $-5^{\circ}$ , with a solution of 15 parts of dry potassium nitrate in 100 of 100% sulphuric acid and the whole allowed to remain at the ordinary temperature during 24 hours.

It is alleged that with longer standing there is formed, little by little, trinitroaniline. The authors have not given the fusion point or made other tests but they note that an analysis for nitrogen gave results corresponding with the calculated value for the trinitroaniline. If, however, we consider that the nitrogen contents of tri- and of tetranitroanilines differ but little (24.56% and 25.65%) one may realize that an examination of impure tetranitroaniline could lead one to believe it to have the composition of the trinitro product.

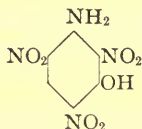
We have sought to prepare the trinitroaniline by the method described by Witt and Witte and, while we have carefully endeavored to follow the instructions given, we have never obtained trinitroaniline but always the tetranitro compound. This was identified not only by the fact that it had the same melting point and that when mixed with this substance the melting point was not lowered, but also because on boiling in the presence of moist acetone it gave 2,4,6-trinitroamidophenol. It may also be remarked here that by this process a very pure tetranitroaniline is immediately obtained.

III. Acetyltetranitroaniline



We prepared this body according to Flürscheim<sup>1</sup> by heating pure tetranitroaniline with acetic anhydride and a little sulphuric acid at a temperature not above  $80^{\circ}$ . After crystallization in glacial acetic acid the tetranitroaniline fuses, with decomposition, at  $169-170^{\circ}$ , cor,

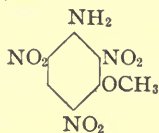
IV. 2,4,6-Trinitroamidophenol



<sup>1</sup> Flürscheim, D. R. P. 241,697, *Chem. Zentr. Bl.*, **1**, 184 (1912); see also Witt and Witte, *oc. cit.*, for the preparation of acetylpicramide.

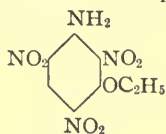
Flürscheim<sup>1</sup> has demonstrated that tetranitroaniline can easily be transformed into trinitroamidophenol, even at the ordinary temperature, if there is added to the acetone solution of it an aqueous solution of sodium acetate. As we have previously shown, apropos of tetranitroaniline, because of water being present with the acetone as well as sodium acetate, the alkaline reaction of this latter ought to accelerate the transformation. We always prepare the trinitroamidophenol by dissolving 100 g. of tetranitroaniline in 600 cc. of acetone with the addition of a little water. As soon as the tetranitro compound is dissolved, we distil off the acetone until the tetranitrophenol crystallizes out; this is then dried, washed with cold alcohol and then recrystallized, at first from alcohol and then from benzene. Melting point 178–179°, cor.

## V. 2,4,6-Trinitroamidoanisol



This product has also been prepared (following Flürscheim) by boiling crude tetranitroaniline with absolute methyl alcohol. The compound obtained is twice crystallized from methyl alcohol. To obtain a pure product it is indispensable that the alcohol be absolute. Melting point 131°, cor.

## VI. 2,4,6-Trinitroamidophenetol



The method of preparation of this substance is similar to that of the trinitroamidoanisol, except that ethyl alcohol is used. We have, however, noticed that when prepared by the use of impure tetranitroaniline very little of the trinitroamidophenetol is obtained, and that that which is formed is also impure. The product is strongly contaminated by a fibrous compound which can be eliminated by crystallization in alcohol-acetone;<sup>2</sup> but then the trinitro-

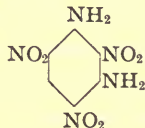
<sup>1</sup> Flürscheim, D. R. P., 243,079, *Chem. Zentr. Bl.*, 1, 620 (1912); *Proc. Chem. Soc. London*, 26, 81.

<sup>2</sup> Many compounds studied by us could be obtained pure with facility by dissolving in warm acetone, then precipitating the compound by the addition of cold alcohol; we employ for this procedure the simplified designation "*cristallisation dans l'alcool-acetone*."



amidophenetol is contaminated by trinitroamidophenol, which is difficult to eliminate by crystallization.<sup>1</sup> While the purification of tetranitroaniline by crystallization from glacial acetic acid is somewhat laborious, we recommend with some insistence the employment of the recrystallized product in the preparation of the trinitroamidophenetol. Melting point, 107°, cor.

VII. 2,4,6-Trinitrometaphenylenediamine



This compound was prepared by Nölting and Collin<sup>2</sup> from diethyl ether, styphnic acid and ammonia in absolute alcohol. They have described the compound as being yellow, crystalline, and fusing only at a high temperature. Barr<sup>3</sup> proceeded as Nölting and Collin did; he described the compound as yellow, fusing above 250°. Blanksma<sup>4</sup> prepared the body from 1,3,2,4,6,-oxymethylchlortrinitrobenzene, but he does not state either the color or the melting point. Meisenheimer and Patzig<sup>5</sup> obtained the compound by the action of hydroxylamine on an alkaline alcoholic solution of symmetric trinitrobenzene; the product principally formed was picramide. Körner and Contardi<sup>6</sup> employed 2,4,6-trinitrodibrom and dichlor benzenes with alcoholic ammonia. They obtained yellow needles fusing above 250°. Flürscheim<sup>7</sup> employed tetranitroaniline and ammonia; melting point, 275°. Van Romburgh and Schepers,<sup>8</sup> by the prolonged action of a nearly saturated aqueous solution of ammonia on 2,3,4,6-tetranitrophenylmethylnitramine, obtained the trinitrometaphenylenediamine as a yellow-brown product fusing above 270°.

In our researches on the substitution of the methylnitroamino group,<sup>9</sup> in the derivatives of tetranitrophenylmethylnitramine, we

<sup>1</sup> Van Duin, *Rec. trav. chim.*, **38**, 89 (1919).

<sup>2</sup> Nölting and Collin, *Ber. d. deutsch. chem. Ges.*, **17**, 260 (1884).

<sup>3</sup> Barr, *Ibid.*, **21**, 1546 (1888).

<sup>4</sup> Blanksma, *Rec. trav. chim.*, **21**, 324 (1902).

<sup>5</sup> Meisenheimer and Patzig, *Ber. d. deutsch. chem. Ges.*, **39**, 2533 (1906).

<sup>6</sup> Körner and Contardi, *Atti R. Accad. dei. Lincei Roma*, **5**, 17, 1, 465 (1908); **5**, 18, 93 (1909); *Chem. Zentr. Bl.*, 1908, II, 47; 1909, I, 1157.

<sup>7</sup> Flürscheim, *loc. cit.*

<sup>8</sup> Van Romburgh and Schepers, *Versl. Konin. Akad. van Wetensch. Amsterdam*, **22**, 293 (1913); Schepers, "Dissertatie," Utrecht, 1913, 41.

<sup>9</sup> Van Duin, *Rec. trav. chim.*, **38**, 89 (1919).

have obtained the trinitrometaphenylenediamine by the action of a concentrated ammoniacal solution of 2,4,6-trinitroanilidophenylmethylnitramine. The product is dark brown and has a melting point of  $295^{\circ}$ , cor. (after  $250^{\circ}$ ,  $10^{\circ}$  per minute). After crystallization in glacial acetic acid, the melting point is raised to  $301^{\circ}$ , cor. (after  $250^{\circ}$ ,  $10^{\circ}$  per minute).

We have also obtained this product by the action of ammonia on the 2,4,6-trinitrodimethylaminophenylmethylnitramine; the compound was dark brown and with a melting point of  $290^{\circ}$ , cor. After crystallization in glacial acetic acid it rose to  $296^{\circ}$ , cor. (here also after  $250^{\circ}$ ,  $10^{\circ}$  per minute). In both cases the color of the product was darkened by recrystallization.

We have obtained the purest trinitrometaphenylenediamine by replacing a halogen atom or an oxyalkyl group by an amino group, which has been achieved by the action of ammonia on trinitro-amido-anisol and -phenetol. That an oxyalkyl group, placed near a similar analogue, can be easily replaced by ammonia has been already shown in the case of the isobutylic ether of the trinitromethylnitraminophenol.<sup>1</sup> Other examples show that this replacement is general for the ethers of trinitroamidophenol and trinitromethylnitraminophenol. In this last case only has there been obtained, by very prolonged action, the aminotritrophenylmethylnitramine, on the side, which imparts a more or less dark brown color to the trinitrometaphenylenediamine. For the preparation of the trinitrometaphenylenediamine there is poured on 10 g. of pure and finely pulverized trinitroamidoanisol or phenetol 80 cc. of a concentrated aqueous solution of ammonia (s. p. 0.90) and the whole left standing for 24 hours at ordinary temperature with frequent agitation; at the end of this time the reaction is complete. The product formed is filtered, freed from ammonia by washing, and boiled with alcohol in order to finally eliminate all traces of the anisol or phenetol which have escaped attack. The melting point is then about  $285^{\circ}$ , cor. After crystallization from glacial acetic acid it is  $287\text{--}288^{\circ}$ , cor. (after  $250^{\circ}$ ,  $10^{\circ}$  per minute). There is thus obtained a trinitrometaphenylenediamine in beautiful yellow crystals with metallic luster.

<sup>1</sup> Van Duin, *Koll. Zeitschr.*, **17**, 123 (1915). The action of a concentrated ammoniacal solution of the ethers of trinitroamidophenol and trinitromethylnitroaminophenol enables us to prepare the corresponding alcohols very pure, which is quite important since easily accessible alcohols do not give crystallizable ethers and they react with tetranitroaniline or tetranitrophenylmethylnitramine to give the ether oxides. See Van Romburgh and Schepers, *loc. cit.*

## NITROGEN DETERMINATION

0.1342 g. of the product gave 33.1 cc. of nitrogen at 17° and 768 mm.

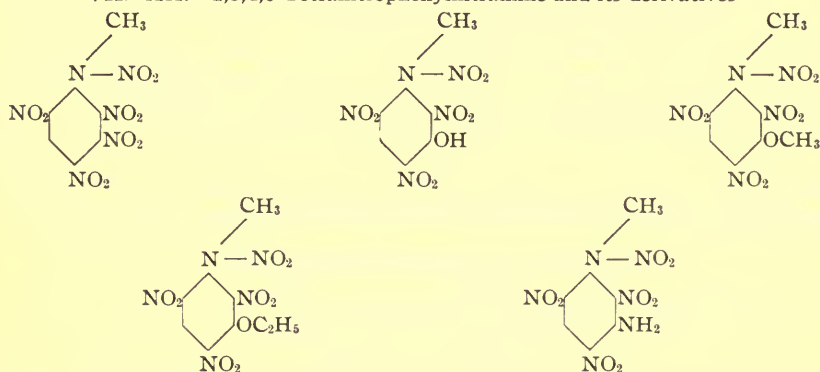
Nitrogen found: 28.78%.

Nitrogen calculated for the trinitrometaphenylenediamine: 28.82%.

In general it may be said that this trinitrometaphenylenediamine is obtained of a more or less dark color when one or two amino groups are introduced into the molecule by means of the derivatives of the methylnitroamino group. It is remarkable that the melting point is higher for the impure compounds; in addition, the recrystallization of the impure compound increases the melting point and at the same time darkens the coloration; it is necessary then to use glacial acetic acid for the recrystallization. The pure product commences to melt without decomposition at 287–288°, cor. (after 250°, 10° per minute); shortly after fusion small gaseous bubbles appear in the clear yellow liquid; this marks the commencement of the decomposition.

It may be said that the impure product having a more elevated melting point and at the same time a dark coloration, may be compared with that which has been observed for the trinitroamido-phenol obtained by replacement of the methylnitramino group in the trinitromethylnitraminophenol by the action of ammonia<sup>1</sup> and removal of the ammoniacal salt. The trinitroamidophenol is brown and melts at 181°, cor., instead of 178–179°, cor.

## VIII-XII. 2,3,4,6-Tetranitrophenylnitramine and its derivatives



In the preparation of these bodies, we have followed precisely the directions given by Van Romburgh and Schepers.<sup>2</sup> The tetranitro-

<sup>1</sup> Van Duin, *Rec. trav. chim.*, **38**, 89 (1919).

<sup>2</sup> Van Romburgh, *Ibid.*, **8**, 273 (1889); Van Romburgh and Scheper, *Versl. Kon. Akad. v. Wetensch. Amsterdam*, **22**, 293 (1913); Schepers, "Dissertatie," Utrecht, 1913.

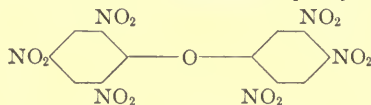
phenylmethylnitramine such as we have used for other experiments was purified by dissolving in warm nitric acid, sp. gr. 1.49, to which we have added a little concentrated sulphuric acid, in order to protect the nitro group in position 3;<sup>1</sup> then, after filtration, we have precipitated the compound with sulphuric acid and have recrystallized in benzene and dried with phosphoric anhydride. Melting point, 146–147°, cor.

The trinitromethylnitraminophenol<sup>2</sup> was obtained by placing the crystallized nitramine in a mixture of sulphuric and nitric acid and heating these with water until solution was complete. This phenol was then precipitated from the solution by chlorhydric acid, filtered, dried in a desiccator over soda and then recrystallized in benzene. Melting point, 183°, cor.

The trinitromethylnitramino-anisol<sup>3</sup> and -phenetol<sup>4</sup> were prepared by boiling the crude nitramine with absolute methyl or ethyl alcohols and then by recrystallization with these alcohols. Melting points: anisol, 96–97°, cor.; phenetol, 98–99°, cor. It is to be remarked that the action of these alcohols when cold is much more rapid with the nitramine than with tetranitroaniline and this shows that there is a much greater mobility of the nitro group in the 3 position; this is in accordance with the results of the tests for stability.

For the preparation of the aminotrinitrophenylmethylnitramine we have followed the method of Schepers<sup>5</sup> but have operated as follows: 140 g. of tetranitrophenylmethylnitramine were introduced little by little into 400 cc. of a 10% aqueous ammoniacal solution during which the reaction vessel was cooled with cold water. After allowing the reaction to take place for one hour, the mixture was poured into 400 cc. of a 10% chlorhydric acid and then the aminotrinitrophenylmethylnitramine formed was filtered. Yield, 120 g.

XIII. 2,4,6,3',4',6'-Hexanitrodiphenylether



<sup>1</sup> Van Romburgh and Schepers, *loc. cit.*

<sup>2</sup> *Ibid.*

<sup>3</sup> *Ibid.*

<sup>4</sup> *Ibid.*

<sup>5</sup> Schepers, *loc. cit.*, 39; this method requires much time for the preparation of large quantities; our preparation is analogous to it.



To purify the product it was at first boiled with alcohol and then crystallized from alcohol-acetone. Melting point,  $188^{\circ}$ , cor.

According to the patent of the Westphälisch-Anhaltische Sprengstoff A. G.<sup>1</sup> the above compound was prepared from the di-, tri-, tetra- and pentanitrodiphenylethers, which had a nitro group in one of the benzene nuclei in the 3 position. As a point of departure we found it best to take the nitrodiphenylether which could be most easily obtained from 2,4-dinitrochlorobenzene or picryl chloride and the *m*-nitrophenol. We have always made use of the 2,4,6,3'-tetranitrodiphenylether which can easily be prepared by following the instructions of the patent.<sup>2</sup> There is thus obtained a compound which melts at  $172^{\circ}$ , cor., after recrystallization from glacial acetic acid. This tetranitrodiphenylether can be easily transformed into 2,4,6,3',4',6'-hexanitrodiphenylether according to the instructions of the patent<sup>3</sup> if it is suspended in concentrated sulphuric acid and the mixture is poured into three to four times its volume of mixed acid (nitric acid, sp. gr. 1.49 and 10% oleum). This mixture is heated to  $100^{\circ}$  and after some time the hexanitrodiphenylether separates out as a solid. If, however, 10 g. of the 2,4,6,3'-tetranitrodiphenylether is suspended in 50 cc. of concentrated sulphuric acid, and this mixture is poured into 150 cc. of mixed acid, composed of 25 cc.  $\text{HNO}_3$ , sp. gr. 1.49, and 125 cc. of 10% oleum, and then heated for an hour or two at  $90^{\circ}$ , there is obtained a product which on recrystallization from acetic acid or toluene melts at  $203\text{--}204^{\circ}$ , cor. This is the pentanitrodiphenylether and not the hexa compound. This penta compound is the 2,4,6,3',4'-pentanitrodiphenylether which is obtained according to the patent at  $110^{\circ}$  from 3,4-dinitrophenylether and the sulphuric-nitric acid mixture.<sup>4</sup>

Analysis: 0.1578 g. of the substance gave 23.90 cc. N at  $18^{\circ}$  under 776 mm.

Nitrogen found: 17.78%.

Nitrogen calculated for pentanitrodiphenylether: 17.73%.

Even if 10 g. of tetranitrodiphenylether was dissolved in 40 cc. of nitric acid, sp. gr. 1.49, and the mixture at  $45^{\circ}$  poured into the mixed acid, formed from 75 cc. of nitric acid, sp. gr. 1.49, and 150

<sup>1</sup> D. R. P. 281,053; *Chem. Zentr. Bl.*, I, 74 (1915). As we have not been able to obtain this patent because of political events, we have followed Escales, "Nitrosprengstoffe," 81.

<sup>2</sup> Following Escales, "Nitrosprengstoffe," Leipzig, 1916, 82.

<sup>3</sup> Escales, *loc. cit.*

<sup>4</sup> D. R. P. 281,053; *Chem. Zentr. Bl.*, 1915, I, 74.



cc. of 10% oleum, and the whole heated to 90° during an hour or two, we still obtain the pentanitroderivative cited above. However we have obtained the 2,4,6,3',4',6'-hexanitrodiphenylether by using more nitric acid (sp. gr. 1.49,) and 30% oleum. The solution of 10 g. of 2,4,6,3'-tetranitrodiphenylether in 40 cc. of nitric acid, sp. gr. 1.49, is brought to 70° in a mixture of 90 cc. of nitric acid, sp. gr. 1.49, and 170 cc. of 30% oleum, and the whole heated during four hours to 90°. There is thus obtained a white solid which melts in a sluggish manner between 240° and 265°; its recrystallization is attended with great loss ( $\approx 50\%$ ); it is best to use nitric acid, sp. gr. 1.49, at first, and then glacial acetic acid. Melting point, 278°, cor. (after 200°, 10° per minute). However, the purest product begins to soften about 265°.<sup>1</sup>

When the filtrate from the recrystallization in nitric acid, sp. gr. 1.49, is poured into water, a precipitate is obtained which melts in a sluggish manner between 215° and 250°; this was at first believed to consist of the 2,4,6,3',4',6'-hexanitrodiphenylether, contaminated with 2,4,6,3',4'-pentanitrodiphenylether. But if this product is nitrated as directed above, that is to say with nitric acid of 1.49 sp. gr. and 30% oleum during four hours at 90°, the melting point does not vary appreciably. This mixture is then probably composed of 2,4,6,3',4',6'-and 2,4,6,2',3',4'-hexanitrodiphenylether.<sup>2</sup> A determination of nitrogen shows that this mass is composed almost entirely of hexanitro derivatives. 0.1462 g. of the substance gives 24.20 cc. nitrogen at 22° under 767 mm.

Nitrogen found: 18.82%.

Nitrogen calculated for pentanitrodiphenylether: 17.73%.

Nitrogen calculated for hexanitrodiphenylether: 19.10%.

We have not tried to isolate from the mixture the hexanitro derivatives, but hope to do this later.

As it appeared important to be able to compare the stabilities, sensitiveness, etc., of 2,4,6,3',4',6'-hexanitrodiphenylether and 2,4,6,2',4',6'-hexanitrodiphenylether, we have attempted to prepare this dipicrylic ether as follows:

At the outset we may say that we are not much surprised that we did not obtain the result, inasmuch as the Griesheim Chemical

<sup>1</sup> According to D. R. P. 281,053, already cited, the melting point is about 269°, not cor.

<sup>2</sup> We do not include the formation of 2,4,6,2',3',6'-hexanitrodiphenylether made by us in our tests long ago for the preparation of 2,4,6,2',4',6'-hexanitrodiphenylether.

Company patented<sup>1</sup> the 2,4,6,2',4'-pentanitrodiphenylether but not the dipicrylic ether, although the latter would be, as an explosive, superior to the former.

1. Ten g. 2,4,6,2',4'-pentanitrodiphenylether were dissolved in 40 cc. of nitric acid, sp. gr. 1.49, and then nitrated during four hours at 90° with a mixture of 90 cc. of nitric acid, sp. gr. 1.49, and 170 cc. of 30% oleum. The initial compound was found unaltered.

2. Two g. of 2,4,6,2',4'-pentanitrodiphenylether were boiled during one-half hour with a mixture of 40 cc. of real nitric acid and 20 cc. of 20% oleum, after which the nitric acid was eliminated.<sup>2</sup> On pouring this mixture into water, no precipitate was obtained, not even a cloud. The penta derivative must then have been oxidized.

3. Nitration with real nitric acid and phosphoric anhydride. On nitrating 2,4,6,2',4'-pentanitrodiphenylether with 30 cc. of real nitric acid and 21 g. of P<sub>2</sub>O<sub>5</sub> during two hours at 40°,<sup>3</sup> the initial product remains unchanged.

4. It is the same if 3 g. of 2,4,6,2',4'-pentanitrodiphenylether are treated with a mixture of 30 cc. of real nitric acid and 30 cc. acetic anhydride, and heated for some time at 30–40°, or allowed to remain for a week at ordinary temperatures; not the least change is observed.<sup>4</sup>

5. If a solution of picryl chloride or bromide<sup>5</sup> is boiled during five hours with silver picrate,<sup>6</sup> there is no transformation.

6. The same result is obtained when 10 g. of picryl chloride are heated seven hours at 100° with 2 g. of silver picrate.

7. A reaction is obtained, however, if given quantities of picryl chloride and silver picrate are heated in absolute alcohol, but this reaction is not of the kind desired. We dissolved 6.8 g. of silver picrate in 230 cc. of boiling absolute alcohol, and then added 5 g. of picryl chloride when the silver chloride commenced immediately to separate. The whole was allowed to boil during ten hours, after which the reaction was apparently complete. The

<sup>1</sup> D. R. P. 81,970; Escales, "Nitrosprengstoffe," Leipzig, 1915, 67.

<sup>2</sup> Picryl bromide appears to have been prepared from 2,4,-dinitrobromobenzene by Jackson and Earle, *Amer. Chem. Journ.*, **29**, 212 (1903).

<sup>3</sup> We do not nitrate at a higher temperature because already at 45° a notable amount of N<sub>2</sub>O<sub>5</sub> from decomposition is formed.

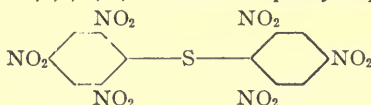
<sup>4</sup> See Franchimont and Friedmann, *Rec. trav. chim.*, **28**, 192 (1908).

<sup>5</sup> Jackson and Earle, *loc. cit.*

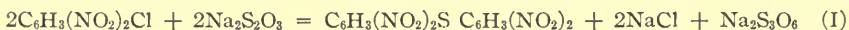
<sup>6</sup> Kast, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **6**, 32 (1911).

silver chloride was filtered and the alcohol distilled. The residue obtained was then extracted twice with water as rapidly as possible<sup>1</sup> in order to eliminate the silver picrate which had not been transformed when the material was recrystallized in absolute alcohol. After several recrystallizations there was obtained a compound melting at 79° which is not lowered by mixing with 2,4,6-trinitrophenetol. The silver picrate has then acted to remove the chlorhydric acid produced from the action of picryl chloride on alcohol. We believe that according to the results which have been enumerated we are warranted in concluding that the formation of 2,4,6,2',4',6'-is impossible because of stereochemical reasons.

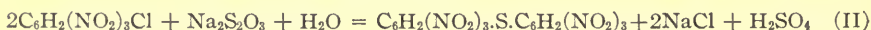
XIV. 2,4,6,2',4',6'-Hexanitrodiphenylsulphide



After having stated<sup>2</sup> that the nitro derivatives of diphenylsulphide can be prepared by the action of alkaline sulphides on chloronitrobenzene, "Sprengstoff A. G. Carbonit"<sup>3</sup> found it could obtain a better yield of the 2,4,2',4'-tetranitrodiphenylsulphide by the action of two molecules of 2,4-dinitrochlorobenzene and two molecules of sodium hyposulphite, according to the following expression:



When, however, they sought to obtain the dipicrylsulphide from picryl chloride by a similar reaction they obtained a dark flocculent mass. From the newer researches of the "Sprengstoff A. G. Carbonit,"<sup>4</sup> the 2,4,6,2',4',6'-hexanitrodiphenylsulphide can be obtained provided but one molecule instead of two of the hyposulphite is employed and the sulphuric acid formed in the reaction is neutralized. The expression for this reaction is:



The yield is about 90%. It is necessary to employ the least excess of hyposulphite in the reaction as decomposition takes place at the same time the color is darkened. The directions of the patent for the formation of hexanitrodiphenylsulphide are precise;

<sup>1</sup> This is for the removal of the trinitrophenetol of hydrolysis but even with boiling water sufficient of the product remains for identification.

<sup>2</sup> Willgerodt, Beilstein II, 1896, 803.

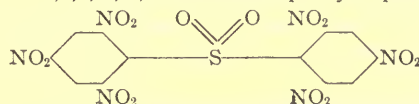
<sup>3</sup> D. R. P. 94,077.

<sup>4</sup> D. R. P. 275,037; *Chem. Zentr. Bl.*, 1914, II, 97. Escales, "Nitrosprengstoffe," 79, 197.

we have never observed decomposition when using pure picryl chloride and the theoretical quantity of hyposulphite; the least excess of hyposulphite, on the contrary, produces decomposition. If one wishes to obtain a crude product which is sufficiently purified by a single recrystallization from alcohol-acetone, it will be prudent to make use of hyposulphite in a quantity a little below the theoretical value.

We have prepared the hexanitrodiphenylsulphide as follows: after the patent of which we have spoken a solution of 20 g. of picryl chloride in 100 cc. of 95% alcohol with 3.8 g. of  $\text{MgCO}_3$  suspended in the solution is boiled in a flask furnished with a reflux condenser. There is then added, little by little, with continual agitation, 10 g. of finely pulverized  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (theory 10.03 g.). New portions of the hyposulphite are added when that which has been introduced has completely reacted. When the reaction is finished the filtered crude product is washed with alcohol, then weak chlorhydric acid, and then water. The yields were 14.45 and 14.65 g. of the hexanitro product, which corresponds to 78.4 and 79.5%. As the patent claims a yield of  $\approx 90\%$  we have tried the reaction with greater quantities of picryl chloride, and using 60 g. of this substance the yield of hexanitrodiphenylsulphide fell to 40 g. or 72.4%. This is why after establishing the fact that the quantity of sulphuric acid corresponds to the weight of hexanitrodiphenylsulphide we have determined the quantity of acid in the filtrate of a preparation made from 20 g. of picryl chloride. From reaction II it is shown that 3.963 g. of sulphuric acid should be formed; we have found 3.721 and 3.725, which corresponds to 93.9% of the theory. In this trial we have anew obtained 79.4% of hexanitrodiphenylsulphide (see above) which ought to produce more sulphuric acid as indicated by reaction II. The appearance of a disagreeable odor of an organic sulphur compound<sup>1</sup> argues also in favor of this interpretation; however, we are not able to indicate the nature of this secondary reaction. The hexanitrodiphenylsulphide is best recrystallized in alcohol-acetone or in glacial acetic acid; the purest product has a melting point of  $233\text{--}234^\circ$ , cor.<sup>2</sup>

XV. 2,4,6,2',4',6'-Hexanitrodiphenylsulphone

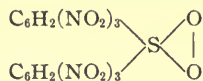


<sup>1</sup> The hexanitrodiphenylsulphide has no odor.

<sup>2</sup> According to Beilstein II, 803, the melting point is  $226^\circ$ , not cor.



Following D. R. P. 269,862<sup>1</sup> of the "Sprengstoff A. G. Carbonit," hexanitrodiphenylsulphide can be transformed into its corresponding sulphone by treating it in suspension in nitric acid, or in a mixture of chromic and acetic acids, with bichromates or oxidizing compounds of manganese. This compound has been assigned a peroxide formula:



but this has been contested by Stettbacher<sup>2</sup> on account of the great stability of the compound. Up to the present we have obtained no other hexanitro derivative of oxidation, following the process indicated, on using other oxidizers such as  $\text{CrO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ . The treatment of the sulphide by potassium permanganate in suspension in nitric or sulphuric acid leaves the material unchanged.

The use of the theoretical quantity of chromic acid having given us satisfactory results, we operated in the following manner: 17.1 g. of hexanitrodiphenylsulphide were put in suspension in 100 cc. of nitric acid, sp. gr. 1.49, then 5 g. of finely pulverized chromic acid were added.<sup>3</sup> The mass was allowed to stand at the ordinary temperature, with agitation from time to time, until the disappearance of the chromic acid, which took about 15 days. During this time the sulphide disappeared also, while there was formed a voluminous, very slightly colored product. This was filtered, washed until acid reaction disappeared, recrystallized in alcohol-acetone, and the sulphone obtained. This was a yellowish white compound, melting at  $307^\circ$ , cor. (after  $250^\circ$ ,  $10^\circ$  per minute).<sup>4</sup>

Analysis: 0.127 g. of substance gives 18.75 cc. nitrogen at  $16^\circ$  and 772 mm.

Nitrogen found: 17.40%.

Nitrogen calculated for hexanitrodiphenylsulphone: 17.22%.

By this process there is obtained a sulphone contaminated by a little sulphide which may be removed by solution in nitric acid of 1.49 sp. gr. In fact, it is necessary to employ as much as 200 cc. of nitric acid for 10 g. of sulphide. On account of the slowness of the reaction we have tried to increase its activity by heat, but we have not obtained any better result with either nitric or acetic acid.

<sup>1</sup> Escales, "Nitrosprengstoffe," Leipzig, 1915, 81, 283.

<sup>2</sup> Stettbacher, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **11**, 115 (1916).

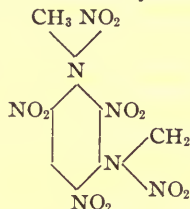
<sup>3</sup> It is strongly recommended that finely pulverized chromic acid be used because the reaction is very slow.

<sup>4</sup> From this melting point, the explosion temperature of  $250$ – $255^\circ$  given in the patent must be inexact.



We entirely agree with the statement of Stettbacher<sup>1</sup> as concerns the constitution of the product. To the argument furnished by this author as to resistance to high temperatures, we wish to add: 1. No iodine is separated when the sulphone, dissolved in glacial acetic acid, is treated with potassium iodide. 2. Sensitiveness to shock: as measured by the drop hammer it is less sensitive than the sulphide<sup>2</sup>; if the sulphone were a peroxide, its sensitiveness would increase.

XVI. 2,4,6-Trinitrodimethyldinitraminebenzene



This compound has been prepared by Van Romburgh from the 1,3-dimethylphenylenediamine,<sup>3</sup> the tetramethylmetaphenylenediamine<sup>4</sup> and the 2,4,6-trinitro-3-methylaminophenylmethylnitramine;<sup>5</sup> by Blanksma<sup>6</sup> from the 1,3-dimethylamine-2,4-dinitrobenzene; and by Blanksma and Meerum Terwogt<sup>7</sup> from the 4,6-dinitrodimethylmetaphenylenediamine with concentrated nitric acid.

We made use of a process analogous to that of Van Romburgh,<sup>8</sup> with the difference that we have not used as our point of departure the monomethyl compound but have employed the dimethylamino-trinitrophenylmethylnitramine which we have obtained from the tetranitrophenylmethylnitramine by using less of the dimethylamine than Schepers.<sup>9</sup> This last preparation was made as follows: To 300 cc. of the 8% aqueous solution of dimethylamine was added, in small portions, with constant cooling by water, 140 g. of tetranitrophenylmethylnitramine and the mixture allowed to stand for half an hour. It was then poured promptly into 250 cc. of 10% chlorhydric acid and the dimethylaminotrinitrophenylmethylni-

<sup>1</sup> Stettbacher, *loc. cit.*

<sup>2</sup> See page 29, Table II.

<sup>3</sup> Van Romburgh, *Rec. trav. chim.*, **6**, 251 (1887).

<sup>4</sup> Van Romburgh, *Ibid.*, **7**, 3 (1888).

<sup>5</sup> Van Romburgh, *Ibid.*, **8**, 280 (1889).

<sup>6</sup> Blanksma, *Ibid.*, **27**, 27, 49 (1907).

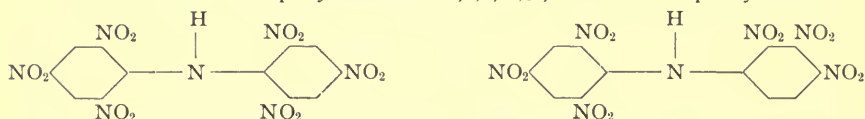
<sup>7</sup> Blanksma with Meerum Terwogt, *Ibid.*, **21**, 291 (1901).

<sup>8</sup> Van Romburgh, *Ibid.*, **8**, 280 (1889).

<sup>9</sup> Schepers, "Dissertatie," Utrecht, 1913, 48; used for 3 gr. of nitramine, 5 gr. dimethylamine.

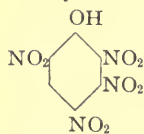
tramine formed was filtered, washed until the disappearance of the acid reaction, and then boiled with alcohol. Yield, 100 g.<sup>1</sup> The crude product was then introduced in small portions into nitric acid, sp. gr. 1.49, and heated to 70–80°, in order to effect the replacement of the dimethylamine group by the methylnitramino group. If sufficient nitric acid is employed there is obtained by recrystallization a very nearly colorless, almost white, product. This crystallization, as stated by Van Romburgh, is best effected in alcohol-acetone. The purified product melts at about 206°, cor. (after 150°, 10° per minute); it is to be remarked that the technical preparation corresponds to that of Van Romburgh who used alkalized metaphenylenediamines.<sup>2</sup>

XVII and XVIII. Dipicrylamine and 2,4,6,2',3',4'-Hexanitrodiphenylamine



For the preparation and properties of these bodies, consult the published memoirs.<sup>3</sup>

XIX. Tetra- We have prepared tetranitrophenol according to  
nitrophenol Blanksma<sup>4</sup> from *m*-nitrophenol and sulphuric-nitric  
acid. The use of real nitric acid is not essential;  
with acid of sp. gr. 1.49 the reaction goes on as described  
by Blanksma. However, it is well not to use at one  
time more than 5 g. of *m*-nitrophenol. By recrystal-  
lization from dry chloroform we have obtained a melting point of  
140°, cor.



### STABILITY

Although the literature of chemistry is quite extended on the subject of the stability of nitroglycerine, guncotton and smokeless powder, it is, on the contrary, very limited as concerns the brisant military nitro explosives and explosives used for industrial purposes. For these last, the stability constants have been established from preliminary trials by the Eighth International Congress of Applied Chemistry<sup>5</sup> on the initiative of Will and Lenze. The German

<sup>1</sup> See Van Duin, *Rec. trav. chim.*, **37**, 111 (1917).

<sup>2</sup> French patent 391,107; Escales, "Nitrosprengstoffe," Leipzig, 1915, 282.

<sup>3</sup> Van Duin and Roeters Van Lennep, *Rec. trav. chim.*, **38**, 358 (1919).

<sup>4</sup> Blanksma, *Ibid.*, **21**, 254 (1902).

<sup>5</sup> *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **7**, 435 (1912); **8**, 345, 370 (1913).

Railway Commission has adopted these constants for nitro explosives.<sup>1</sup> The reason for much of the delay in the examination of nitro explosives is due to the peculiar characteristics of the nitro compounds, picric acid and trinitrotoluene. Verola<sup>2</sup> has shown that trinitrotoluene may be maintained during 100 hours at 100° without its showing any alteration; the setting point, 80.7°, does not change. We have no similar data for picric acid at our disposal; we notice only that in Holland picric acid (and the same may be said of trinitrotoluene) must respond to such a trial as the following: 10 g. heated at 95° during three hours did not give off the least trace of nitrogen oxides. Picric acid endures this test very well; it may even be repeated during several weeks by heating it each day during eight hours to 95°, without the least nitrous vapor making its appearance.

But the question of the stability of brisant nitro explosives entered on a new phase with the employment of nitro compounds containing one or more methylnitramino or mobile nitro groups. Of the first group, that of the nitramines, it is not necessary to again take count. The trinitrophenylmethylnitramine, used nearly exclusively at the present time, is very stable when in a sufficiently pure condition. It is quite otherwise with tetranitrophenylmethylnitramine and tetranitroaniline, which have been described as very stable,<sup>3</sup> they being, however, rapidly decomposed even if they are very pure.<sup>4</sup> This is the more remarkable if we recall that tetranitroaniline is more stable at 70° than nitroglycerine, while at the ordinary temperature the contrary is true. The Nobel Dynamite Factory at Avigliana preserves today 200 g. of the nitroglycerine which was prepared for the first time in 1848 by Sobrero; the nitrogen content of this specimen has not varied up to the present, nor has it shown the least trace of acid.<sup>5</sup> Tetranitroaniline, on the contrary, resists well tests of stability at 71°<sup>6</sup> while in different

<sup>1</sup> Escales, "Ammonsalpetersprengstoffe," Leipzig, 1909, 120.

<sup>2</sup> Verola, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, 7, 211 (1912); Escales, "Nitrosprengstoffe," Leipzig, 1915, 297.

<sup>3</sup> Flürscheim, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, 8, 185 (1913).

<sup>4</sup> The communication of Claessen in Holland patent no. 5,240, stating that the 2,3,5,6-tetranitro-anisol is notably more stable than the trinitrophenylmethylnitramine, ought to be regarded as inexact. This conclusion was based solely on the high temperature of inflammation, 300°.

<sup>5</sup> Escales, "Nitroglycerine and dynamite," Leipzig, 1908, 3.

<sup>6</sup> Kast, "Spreng- und Zündmittel," 1909, 952.

countries a well determined decomposition has been observed at ordinary temperatures after 9 weeks.

In our researches on the stability of brisant nitro explosives, we have not determined whether these explosives respond to the tests of stability employed for safety explosives. These tests are of value for technical products, but the Abel test, in which is observed the first disengagement of nitrous vapors, is too sensitive for these technical products.<sup>1</sup> This test is made in duplicate: 10 g. of the explosive are heated in flasks of determined dimensions during 48 hours at 75°, after which there should not be produced the least sign of decomposition as shown by the appearance or odor.<sup>2</sup> For nitro compounds, it is further stipulated if changes are produced the sensitiveness to shock should be determined on a sample in which the change is most marked.<sup>3</sup> As we have tried chemically pure compounds only, we have observed, following Abel, whether or not a change was produced by them in starch-zinc-iodide papers moistened with glycerine solution. The eventual presence of nitrogen oxides thus shown can be due only to the decomposition of the explosive because of the purity of the same, and this gives a good idea of the stability. In our stability trials we have first sought to ascertain if the explosive responds to the test applied in Holland to picric acid and to trinitrotoluene, that is to say, if on heating 10 g. to 95° during 3 hours the least decomposition is to be observed. If the result of this test was good, the substance was then heated during 30 days at the rate of 8 hours per day. If after this period the material showed no change, the test was stopped since its prolongation seemed to be without significance. The term of 30 days was fixed upon arbitrarily. If the explosive failed to pass that test, a determination of its stability was made at lower temperatures.

In the tests of stability at 32°, 50°, 95°, 10 g. of the substance were heated in flasks of the kind specially used for determining the stability of smokeless powder and guncotton. These flasks have a capacity of 29.3 cc. ( $\pm 3$  cc.) and a height measured just to the stopper of 46.1 mm. ( $\pm 2$ ); they ought to pass the test called the "ether test," which consists in placing 10 cc. of ether in a flask and weighing the whole; after 24 hours of rest at the ordinary tem-

<sup>1</sup> Lenze, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **4**, 303 (1909).

<sup>2</sup> *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **8**, 370 (1913).

<sup>3</sup> Escales, "Ammonsalpetersprengstoffe," 120.



perature the diminution in weight ought not to surpass 100 mg. For the trials at other temperatures we have employed tubes 16 cm. in length and 17 mm. in diameter, with a 2 cm., well ground, glass stopper; these tubes passed the ether test; they were placed in water baths at constant temperature, which is not possible with flasks. The zinc-iodide-starch paper was prepared as follows: 100 cc. of water containing 4 g. of starch and 20 g. of zinc chloride were boiled during 2 hours. 2 g. of zinc iodide and a liter of water were then added and the whole filtered. In this solution strips of Schleicher and Schüll's No. 590 filter paper were soaked during one minute and then dried in darkness and preserved in hermetically closed boxes. For use the paper thus prepared is moistened with a 10% solution of glycerine by placing a drop on the lower part. We have described the preparation of this zinc-iodide-starch paper because there is attributed to it a certain importance<sup>1</sup> and this is an essential thing for the comparison of these tests. We give below results obtained with the different explosives and data of the literature, the compounds, prepared according to the methods described in the preceding pages, being in a state of great purity.<sup>2</sup>

1. The following compounds have responded to the tests described in the preceding pages, which consist in heating 10 g. of the material to 95° without the least trace of nitrous acid having been disclosed. These are: Trinitrophenylmethylnitramine, trinitroamidophenol, -anisol and -phenetol, trinitrometaphenylenediamine, trinitromethylnitraminophenol, aminotrinitrophenylmethylnitramine, hexanitrodiphenyl sulphide and sulphone, and dipicrylamine. For each of these substances the test has been continued during 30 days at a rate of 8 hours per day without the least change. On account of the great importance of the trinitrophenylmethylnitramine to our modern explosives industry,<sup>3</sup> we have continued the test for this last during 185 days, without having observed the least decomposition. In the case of the trinitrodimethyldinitraminobenzene, one flask has shown a reaction after three days, while after four days four flasks have shown a decomposition.

2a. *Tetranitroaniline*. According to Flürscheim,<sup>4</sup> it is easy to

<sup>1</sup> See *Zeitschrift f. d. ges. Schiess- und Sprengstoffw.*, 9, 293 (1914); there is given, with details, the preparation of the paper employed in England.

<sup>2</sup> For more details, see Van Duin, "Dissertatie," Utrecht, 1918, 76-84.

<sup>3</sup> See Van Duin and Brackmann, *Chem. Weekbl.*, 16, 501 (1919).

<sup>4</sup> Flürscheim, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, 8, 185 (1913).



prepare a product which will not cause coloration of the reagent paper after 60 minutes, exposure at 71°; the same author indicates that the stability at 120° equals that of tetryl. However, Stettbacher<sup>1</sup> has already shown that the purest tetranitroaniline decomposes after 8 days, this being attributed to the reaction between the orthonitro and the amino groups.<sup>2</sup>

Test at 70°. After two hours' heating, no trace of nitrogen oxide was observed; this is also the case after three hours.

Test at 60°. No decomposition after 18 hours, nor even after 26 hours.

At 50°. We have heated the specimens day and night; the seventeenth day two out of four flasks gave a positive reaction.

At 32°. The reagent paper has shown the presence of nitrogen oxide compounds after 9 weeks.

2b. *Acetyltetranitroaniline*. Special stability tests have not been made on this. We mention it only because the product, purified as described above, shows an acid decomposition after two months of preservation in a well stoppered flask.

2c. *Tetranitrophenylmethylnitramine*. Stettbacher<sup>3</sup> has presented the hypothesis that this compound would be more stable than tetranitroaniline. As will be shown, precisely the contrary is true.

Stability at 60°. Of four flasks tested, two have given after one hour a feeble reaction with the zinc-iodide-starch paper; after four hours the four flasks have each given a strong reaction.

Stability at 50°. After 15 days the four samples have given a decided reaction.

Stability at 32°. Two flasks have given a positive reaction after four weeks and the others after five weeks.

We insist that it is not advisable to introduce the reagent paper into the tubes used for the stability test of tetranitro compounds, which easily react when warmed with water vapor. This is why we have made our tests in this search of the nitrogen oxide compounds by introducing zinc-iodide-starch paper into the test tubes from time to time and keeping them there for but about 30 seconds. The same error attends the use of other reagents which have been

<sup>1</sup> Stettbacher, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **11**, 114 (1916).

<sup>2</sup> Stettbacher, *loc. cit.*; Escales and Stettbacher, "Initialexplosivstoffe," Leipzig, 1917, 250, 254.

<sup>3</sup> Stettbacher, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **11**, 114 (1916).

proposed for testing the stability of compounds easily yielding nitrogen oxide derivatives in the presence of water vapor.<sup>1</sup>

2d. *Tetranitrophenol*. We have not determined the stability of this compound except at 70°, on account of the difficulty in obtaining the well purified product. The results obtained are otherwise sufficient for all our purposes. The tetranitrophenol appears to behave like other tetranitro compounds. The presence of nitrogen oxides was not shown, however, after maintaining the tetranitrophenol at 70° during three hours, but after four hours the reaction was positive.

2e. *2,4,6,3',4',6'-Hexanitrodiphenylether*. In spite of the presence of the mobile nitro group, no decomposition had taken place after heating for three hours at 95°; after eight hours the reaction was positive.

2f. *2,4,6,2',3',4'-Hexanitrodiphenylamine*. As this product is difficult to obtain, we have simply observed whether its stability is markedly diminished by the replacement of an immobile nitro group in the dipicrylamine by a mobile group. It is in effect thus: A strong reaction with the zinc-iodide-starch paper was observed after heating one hour at 95°.

3. *Trinitromethylnitramino-anisol and -phenetol*. The stability of this compound is markedly less than that of the corresponding phenols; we have definitely proved our several preparations. The anisol after heating for one hour at 90° gave no reaction, but after two hours the reaction was positive. At 80° the test is negative during 24 hours, positive after 26 hours. On heating the flasks to 70° at the rate of eight hours per day, a positive reaction was observed after 15 days. At 50° at constant heat, 20 weeks were needed to render the reaction positive. With phenetol, there was no reaction after one hour's heating at 90°, but a marked reaction after two hours. The reaction is much more manifest than that of anisol. At 30°, a reaction after 12 hours (none after 10); at 70°, reaction after 7 hours' heating, at the rate of 8 hours per day; and at 50°, after 20 weeks. It should be noted that we have observed a less stability for the phenetol among our preparations.

We ought also to observe that the nitrogen oxides produced in our tests of stability of tetranitro compounds come from the

<sup>1</sup> See Guttman, *Zeitschr. f. angew. Chem.*, 1897, 265; Egerton, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, 8, 390 (1913). These authors have worked with solutions of diphenylamines, especially naphthylamine and dimethylaniline, which also contain water.

compounds themselves, and not from the reaction between the nitro product and the moisture of the paper. This is clearly shown by the test made with three tubes each containing 10 g. of tetranitroaniline heated in a water bath at 70°. The first tube was tested after one hour and it gave no positive reaction; after two hours the second tube was also examined; neither of the two tubes gave a positive reaction, but after three hours all three tubes gave a positive reaction. It is incontestable that if the reagent paper had left a little moisture in the first tube, its positive reaction should have been produced before the second and third trials. Furthermore, the presence of nitrogen oxide compounds can be disclosed for a very pure specimen of tetranitrophenylmethylnitramine, preserved in a sulphuric acid desiccator at a temperature of 32°.

### CONCLUSIONS

*a.* It has been shown that if the chemically pure tetranitro compounds 2,3,4,6- decompose more rapidly at an elevated than at ordinary temperature, this may be attributed to the separation of nitrous acid from nitro group 3. If tetranitroaniline be compared with tetranitrophenylmethylnitramine, it is seen that the most active nitro groups have also the least stability. The conception of Stettbacher already mentioned, according to which the nitrous acid disengaged in the decomposition of tetranitroaniline proceeds from a reaction between the amido and the ortho nitro groups, is inexact, for the trinitrometaphenylenediamine and the aminotrinutrophenylmethylnitramine, which ought easily to undergo this species of decomposition, are very stable compounds.

Furthermore, the fact that dipicrylamine is very stable and that 2,4,6,2',3',4'-hexanitrodiphenylamine is not so, proves that the mobile nitro group is the cause of the instability in nitro compounds possessing such a mobile group. The great importance of the relative mobility of this nitro group is shown by the test of 2,4,6,-3',4',6'-hexanitrodiphenylether, which houses the nitro group in 3, and is much less mobile than the 2,4,6,2',3',4'-hexanitrodiphenylamine.

*b.* Tests of trinitrophenylmethylnitramine and trinitrodimethyldinitraminobenzene show that the influence on the stability of the methylnitramino group, which is much less than that of a mobile nitro group, is also unfavorable. When the products are sufficiently pure, the introduction of these two methylnitramino groups pre-

sents no difficulty. In consideration of the tests made on the tetryl it will be advisable in this preparation not to make use of too little nitric acid.

c. We cannot explain completely the trinitromethylnitramino-anisol and-phenetol from the point of view of absolute, as compared with relative, stability. We believe also that a generalization based on the instability of these compounds to light is not possible; the very stable trinitromethylnitraminophenol is the more sensitive to light. It is possible in these compounds that the methylnitramino group becomes very mobile. However, it is not possible to establish this for the basic agents employed to produce the substitution of the oxyalkyl group.

One can obtain a fair idea of the value of the mobility of the nitro group by a determination of the heat of combustion. This determination should be made, on the one hand, for:

2,4-Dinitrophenylmethylnitramine.

2,4,6-Trinitrophenylmethylnitramine.

2,3,4,6-Tetranitrophenylmethylnitramine.

and on the other hand for:

2,4-Dinitroaniline.

2,4,6-Trinitroaniline.

2,3,4,6-Tetranitroaniline.

It would suffice to give greater mobility to the fourth nitro group, instead of to the nitramine in the 3 position, to augment the value of the heat of combustion which will be greater for the passage of the trinitramine to the tetranitronitramine than for the passage of the trinitroaniline to the tetranitroaniline. The series consisting of di-, tri- and tetranitrophenol is also interesting from this point of view; if we note that 0.2 g. of tetranitrophenol detonates in the determination of its initial explosion temperature it is evident that the determination of its heat of combustion and probably also of the tetranitrophenylmethylnitramine cannot be effected in the explosion calorimeter.

#### DETERMINATION OF THE INITIAL EXPLOSION TEMPERATURE

This constant of explosives is the temperature to which, through a well determined elevation of temperature (see below) it is brought to explode or inflame. As a means of ascertaining the degree of purity of crystallizable compounds, this constant is not of great



value; for this purpose the fusion and decomposition points are already indexes; if then determinations are made of the initial explosion temperature, it is to obtain an indication of the same value; for while the decomposition and explosion temperatures are not the same thing, it is not infrequently the case with the brisant nitro explosives to have the same figure for the two. Only the circumstances which determine the initial explosion temperature render it necessary to use a larger quantity of the substance (up to 0.5 g.) to give this constant some value, because one can better observe the decomposition phenomena at high temperature.

Though it has not been possible to determine if the influence of stabilization is as great for brisant nitro explosives as for guncotton,<sup>1</sup> it appears to us that it is still effective. Guncotton as ordinarily stabilized has an initial explosion temperature of 180°, but this may fall to 120°, and even lower if the guncotton is insufficiently stabilized.<sup>2</sup> Trinitromethylnitraminophenol, when pure, has an initial explosion temperature of 188°; Van Romburgh<sup>3</sup> has, however, produced an explosion at 120° by heating the impure compound in an oil bath. But the published information on decomposition at high temperature<sup>4</sup> fails to show the part played by the decomposition products which are formed.<sup>5</sup>

As has already been said, it is indispensable in the determination of the initial explosion temperature to hold to precise experimental conditions in order to obtain comparable results. We have made our determinations according to generally accepted methods.<sup>6</sup> In method A, the substance is heated above 100° at the rate of 20° per minute, and in method B (employed in Holland for smokeless powder and guncotton) the elevation of temperature above 100° is at the rate of 5° per minute.<sup>7</sup> The temperatures found by method B are evidently lower than those of method A. We, however, give the preference to heating at the rate of 5° per minute, because thus we can better take account of the manner in which the materials behave at high temperatures. Certain substances which give a

<sup>1</sup> Precise trials have not again been made on this subject.

<sup>2</sup> Brunswig, "Explosivstoffe," 1909, 28.

<sup>3</sup> Van Romburgh, *Versl. Kon. Akad. Van Wetensch. Amsterdam*, **23**, 1314 (1915).

<sup>4</sup> See Hoitsema, *Zeitschr. f. physik. Chem.*, **21**, 137 (1896).

<sup>5</sup> Brunswig, "Explosivstoffe," **29**, 154 (1909); the information for guncotton will be found in the bibliography.

<sup>6</sup> Marshall, "Explosives," etc., 1915, 588; Escales, VI, 427.

<sup>7</sup> See also Brunswig, "Explosivstoffe," 1909, 28.



more or less precise initial explosion temperature when heated at the rate of 20° per minute, do not give the same phenomenon when heated at the rate of 5° per minute because the decomposition is more progressive. In method A we have used 0.2 g. (the quantity can vary from 0.2 to 0.5 g.) and in method B we have used the prescribed weights, that is to say, 0.1.

TABLE I  
Table of initial explosion temperatures<sup>1</sup>

NAME OF EXPLOSIVE	TEMPERATURE OF EXPLOSION METHOD A	TEMPERATURE OF EXPLOSION METHOD B	REMARKS
	Degrees	Degrees	
Trinitrotoluol.....	321	304	
Picric acid.....	316	309	
Trinitrophenylmethylnitramine.....	196	187	3 out of 12 with progressive decompn. (B)
Tetranitroaniline.....	247	237	2 out of 6. id.
Trinitroamidophenol.....	250	231	4 out of 6. id.
Trinitroamidoanisol.....	254	238	
Trinitroamidophenetol.....	257	236	4 out of 6. id.
Trinitrometaphenylenediamine.....	335	320	
Tetranitrophenylmethylnitramine....	175	162	
Trinitromethylnitraminophenol.....	197	188	
Trinitromethylnitraminoanisol.....	198	187	1 out of 6. id.
Trinitromethylnitraminophenetol....	202	192	4 out of 6. id.
Aminotrinitrophenylmethylnitramine.	201	190	
2,4,6,3',4',6'-Hexanitrodiphenylether.	318	313	1 out of 6. id.
Hexanitrodiphenylsulphide.....	319	302	
Hexanitrodiphenylsulphone.....	308	297	
Trinitrodimethyldinitraminobenzene .	214	197	
Dipicrylamine.....	258	250	3 out of 6 not observed; the substance is progressively decomposed. (B)
2,4,6,2',3',4'-Hexanitrodiphenylamine	287	282	
Tetranitrophenol.....	251	245	According to A, detonation.

<sup>1</sup> For more detailed information, see Van Duin, "Dissertatie," Utrecht, 1918, 89-98.

The compounds have been purified as for the tests for stability; in addition, they were pulverized in advance. We have used those which passed a sieve of 361 openings per sq. cm. with a diameter of wire of 0.195 mm. and which have remained on a sieve of 529 openings with a diameter of wire of 155 mm. In this way our compounds have been pulverized to a uniform fineness, which offers an advantage in that they occupy very nearly the same space in the

reaction tubes. As regards the apparatus, we have used for method A apparatus of the prescribed dimensions and filled with "Woods" metal only, but instead of three we have heated but two tubes at a time. For method B, we have made use of the Hollandaise apparatus which is a little larger and filled with oil. We doubt, however, the importance of these dimensions. We remark again that the metallic bath was not agitated, while the oil bath was, and this explains the more concordant results obtained under the latter conditions.

Below will be found the values obtained, presented in tabular form. The temperatures given are corrected, and are the mean of six determinations or less.

### CONCLUSIONS

a. In the determination of initial explosion temperatures it is recommended that both methods A and B be used, even though one apprehends that the behavior of the explosives at high temperature is different for each case. It is thus, for example, that one perceives that tetryl decomposes when heated at the rate of  $5^{\circ}$  per minute, while nothing is observed when the temperature rises at the rate of  $20^{\circ}$  per minute. Tetranitrophenol, treated by method B, is inflamed, and ordinarily the phenomenon is vivid, while method A produces generally a detonation. With the tetranitrophenyl-methylnitramine, it never results in detonation but a good explosion with much flame; we suppose, however, that this compound in a sufficiently great quantity, will undergo detonation.

b. It is not possible to combine the stability and the initial explosion temperature by saying that of two explosives that having the highest initial explosion temperature has the greatest stability.<sup>1</sup> For proof of this, one should compare the relative figures given for the stability and those for the initial explosion temperature.

c. For explosives which decompose on fusion, the temperatures of decomposition and initial explosion are generally nearly the same.<sup>2</sup> If the product does not decompose on fusion it is not possible to say *a priori* what the initial explosion temperature is. Thus we have it that tetranitrophenylmethylnitramine fuses at  $147^{\circ}$ ; and the

<sup>1</sup> See Claessen, Application for patent (Holland) No. 5,240, Aug. 17, 1915.

<sup>2</sup> It follows that the figures given for hexanitrodiphenylsulphone, *viz.*, melting point  $306^{\circ}$  cor., initial explosion temperature  $250-255^{\circ}$ , are erroneous (Escalaes, VI, 81). This is probably the initial explosion temperature of the mixture of 2,4,6,3',4',6'- and 2,4,6,2',3',4'-hexanitrodiphenylether which is formed in the preparation.

tetranitrophenol at 140°; the initial explosion temperature of the latter is 250° and that of the former 175°, yet these two compounds are excellent examples of tetranitro derivatives.

#### SENSITIVENESS TO MECHANICAL EFFECTS

Of the four methods which have been employed in the test of an explosive by shock,<sup>1</sup> notably the test by the impact machine, the test by fulminate detonators,<sup>2</sup> the test of firing and the test of friction in an unglazed porcelain mortar,<sup>3</sup> the first two are the more important because they enable one to class the explosives more rigorously. Of these two methods, that of the impact machine is the more precise. This is why we have applied it to the examination of nitro compounds. Will,<sup>4</sup> Lenze,<sup>5</sup> Mettegang,<sup>6</sup> Bichel,<sup>7</sup> Kast,<sup>8</sup> Zschokke,<sup>9</sup> have made researches having for their object the construction of apparatus with which to obtain certain and precise results and also to determine the conditions to which very close attention should be given during the execution of the tests. This information on these matters will be found in the works of Lenze cited above, and in those of Kast, which give particular instructions.

Concerning apparatus and the conforming to the "surface constant of the explosive," we refer to Kast, "Anleitung," etc., 1908, 1015, and Escales, "Nitrosprengstoffe," 422. The surface of the stamps is, according to these authors, 1½ sq. cm., but this value is not international. Thus the dimension of the apparatus of "The American Bureau of Mines" is 0.785 sq. cm.<sup>10</sup> of surface, while that proposed at the Eighth International Congress of Applied Chemistry is 1.27 sq. cm.<sup>11</sup> It was proposed further to make ten tests of impact, taking picric acid as the standard for comparison, all of these measurements to be made in the same apparatus with the weight of the finely pulverized substance varying from 0.05 to 0.01 g.<sup>12</sup>

<sup>1</sup> Will, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **1**, 209 (1906).

<sup>2</sup> Bichel, "Glückauf," **41**, 1194 (1905).

<sup>3</sup> See Kast, "Spreng- und Zündstoffe," Braunschweig, 1909, 1017.

<sup>4</sup> Will, *loc. cit.*

<sup>5</sup> Lenze, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **1**, 287 (1906).

<sup>6</sup> Mettegang, *Ibid.*, **1**, 293 (1906).

<sup>7</sup> Bichel, *Ibid.*, **3**, 403 (1908). *Marinerundschau*, **16**, 1345 (1905).

<sup>8</sup> Kast, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **4**, 263 (1909).

<sup>9</sup> Zschokke, "Militärische Sprengtechnik," 1911.

<sup>10</sup> Marshall, "Explosives, Their Manufacture, Properties, Test and History," 1915, 345

<sup>11</sup> *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **8**, 370 (1913).

<sup>12</sup> According to Kast, there is invariably employed at the "Militärversuchsanstalt" of Berlin, 0.04 g. of the substance with a stamp surface of 0.5 sq. cm.

It is also to be noted that Wöhler and Matter<sup>1</sup> have constructed a form of impact machine (Fallpendel) for testing initiating explosives which is made in such a manner as to permit the compounds resulting from the explosion to escape after detonation; this is necessary, for otherwise the stamps are frequently broken.

On the subject of the sensibility of explosives in general, van't Hoff<sup>2</sup> has already pointed out that definite atomic combinations show always a special sensitiveness. Further, the quantity of energy set free during the explosion also plays a part. For compounds of analogous constitution, the sensitiveness appears to be a measure of the augmentation of the energy set free, while strongly endothermic compounds, such as mercury fulminate, lead azide, etc., are as a rule very sensitive. However, there intervene also unknown factors which one may expect to find among the explosives which are the more sensitive of the exothermic compounds, such as lead picrate.<sup>3</sup> Will<sup>4</sup> has made the most interesting research on this subject on the three isomeric trinitrotoluenes. He has shown that the 2,3,4- isomer is the most sensitive; this is because it possesses the most mobile nitro group in the 3 position, and consequently possesses the greatest energy.<sup>5</sup> Then follows the 3,4,6- isomer and finally the symmetric trinitrotoluene which has no mobile nitro group.

In our tests, we have used the apparatus described by Kast with a stamp surface of 5 sq. cm.; we have used only a single apparatus because we have had no others at our disposal. We have operated at a temperature of 19° to 23°;<sup>6</sup> in order to be sure of the constancy in temperature of the stamps, we have proceeded as follows: Four stamps were employed in a determined order and washed in acetone, volatilized rapidly, and then permitted to remain during the previous operation. The purity of the explosives tested was the same as those whose stability and initial explosion temperature were measured. But as the physical state has an influence the com-

<sup>1</sup> Wöhler, *Zeitschr. f. angew. Chem.*, **24**, 2089 (1911).

<sup>2</sup> Van't Hoff, "Vorlesung über theor. und physikal. Chem.," 1900, III, 95.

<sup>3</sup> Dupre, "Mem. des Poudres et Salpêtres," **11**, 94 (1901). See also Brunswig, "Explosivstoffe," 1909, 7-14.

<sup>4</sup> Will, *Ber. d. deutsch. chem. Ges.*, **47**, 704 (1914).

<sup>5</sup> On this, Will has not published information; he mentions only that the three isomers have almost the same heat of combustion, which is about 3660 calories.

<sup>6</sup> Because of the bad location of our impact machine we have not operated between 18° and 20° (Kast, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **4**, 263 (1909), or between 15° to 20° (Escales, "Nitrosprengstoffe," Leipzig, 1915, 423).



pounds were formed by slow and tranquil crystallization which has given, in nearly all cases, hard crystals which were then pulverized. Only the trinitroamidophenetol and the trinitromethylnitraminophenetol have failed to give hard crystals; these were always more or less elastic. Finally, the pulverized explosives were dried during 24 hours over fragments of potash. We have preferred potash to the usual calcium chloride because certain of these explosives were recrystallized from glacial acetic acid.

For the tetranitrophenylmethylnitramine we have made a final crystallization in benzene, with agitation, for the crystals obtained by slow crystallization are very hard and their pulverization appears too dangerous on account of the great sensibility which we attribute to this body. It is true that we have pulverized this compound under a glass with the aid of a horn spatula, but we have not sieved it because the small particles agglutinate into boulets.

Since constancy in the thickness of the layer of explosive is of great importance, we have measured the materials in a large capsule containing on an average, when used for tetryl, about 42 mg. It is evident that the quantities of the different materials measured in this manner will not be the same. The weights are given for each substance tested in the tables which follow. After having obtained uniformity in the degree of fineness of the materials, we have sieved them through a sieve of 1330 apertures per sq. cm., with a diameter of wire of 0.105 mm. Since tetryl appears more and more to be accepted as a standard, we have taken this substance as the standard of comparison and we have determined the results by measurements repeated each day. In the tables which follow we have recorded these values beside those for the explosive tested the same day. The determinations of all of these substances have been made on two different days; the two values will be found in the table.

We have at first employed in our experiments a weight of 2 kg., but since for about 8 explosives the maximum height of fall established for this weight (60 cm.<sup>1</sup>) is not sufficient, for these explosives we have used a weight of 10 kg.<sup>2</sup> Following Kast, we have determined the maximum height of fall for which there is no explosion in an uninterrupted series of 6 trials, and the minimum height of fall, for which there is always an explosion, with an uninterrupted

<sup>1</sup> We wished to keep to the maximum height which Kast states was followed in his researches.

<sup>2</sup> We had only weights of 2 and 10 kg. at our disposal.

TABLE II  
Weight of plunger 2 kg. Temperature 19–23°

NAME OF EXPLOSIVE	MEAN QUANTITIES OF SUB- STANCE IN CAPSULE IN MG.	MAX. HT. 0 TO 6 CM.	MIN. HT. 6 TO 6 CM.	MAX. HT. 0 TO 6 CM., <sub>1</sub>	STANDARD (TETRYL)	MIN. HT., 6 TO 6 CM.
Trinitrotoluene.....	39	> 60	> 60	51	..	> 60
..	..	> 60	> 60	49	..	> 60
Picric acid.....	36	> 60	> 60	51	..	> 60
..	..	> 60	> 60	49	..	> 60
Tetranitroaniline.....	39	55	> 60	53	..	> 60
..	..	54	> 60	51	..	> 60
Tetranitroamidophenol.....	46	> 60	> 60	49	..	> 60
..	..	> 60	> 60	49	..	> 60
Tetranitroamidoanisol.....	37	> 60	> 60	49	..	> 60
..	..	> 60	> 60	49	..	> 60
Tetranitroamidophenetol.....	37	> 60	> 60	49	..	> 60
..	..	> 60	> 60	49	..	> 60
Tetranitrometaphenylenediamine....	33	> 60	> 60	51	..	> 60
..	..	> 60	> 60	50	..	> 60
Tetranitrophenylmethylnitramine....	25	19	36 <sup>1</sup>	53	..	> 60
..	..	19	36 <sup>2</sup>	51	..	> 60
Trinitromethylnitraminophenol.....	42	33	> 60	51	..	> 60
..	..	30	> 60	50	..	> 60
Trinitromethylnitraminoanisol.....	39	> 60	> 60	51	..	> 60
..	..	> 60	> 60	51	..	> 60
Trinitromethylnitraminophenetol....	34	> 60	> 60	51	..	> 60
..	..	> 60	> 60	51	..	> 60
Aminotrinitrophenylmethylnitramine.	42	45	> 60	51	..	> 60
..	..	43	> 60	51	..	> 60
2,4,6,3',4',6'-Hexanitrodiphenylether.	39	35	> 60	50	..	> 60
..	..	32	> 60	53	..	> 60
Hexanitrodiphenylsulphide.....	47	36	> 60	49	..	> 60
..	..	39	> 60	51	..	> 60
Hexanitrodiphenylsulphone.....	38	43	> 60	49	..	> 60
..	..	43	> 60	51	..	> 60
Trinitrodimethyldinitraminobenzene.	40	21	37 <sup>3</sup>	49	..	> 60
..	..	26	36 <sup>4</sup>	51	..	> 60
Dipicrylamine.....	38	49	> 60	50	..	> 60
..	..	49	> 60	53	..	> 60
2,4,6,2',3',4'-Hexanitrodiphenylamine	41	47	> 60	50	..	> 60
..	..	44	> 60	53	..	> 60
Tetranitrophenol.....	40	26	45 <sup>5</sup>	53	..	> 60
..	..	28	52 <sup>6</sup>	51	..	> 60

<sup>1</sup> and <sup>2</sup>. All six explosions complete with flames.<sup>3</sup> All explosions complete; only four with flames.<sup>4</sup> All explosions complete with flames.<sup>5</sup> and <sup>6</sup>. All explosions complete with flames, very strong detonation and great flame.

series of 6 trials.<sup>1</sup> All these results are recorded in Tables II and III.

TABLE III  
Weight of plunger 10 kg. Temperature 19–24°

NAME OF EXPLOSIVE	MEAN QUANTITIES OF SUB- STANCE IN CAPSULE IN MG.	MAX. HT. 0 TO 6 CM.	MIN. HT. 6 TO 6 CM.	MAX. HT. 0 TO 6 CM.	STANDARD (TETRYL)	MIN. HT. 6 TO 6 CM.
Trinitrotoluene.....	39	24	24	14	..	24
	..	24	24	14	..	24
Picric acid.....	36	18	24	14	..	24
	..	19	24	14	..	24
Trinitroamidophenol.....	46	24	24	14	..	24
	..	22 <sup>1</sup>	24	14	..	24
Trinitroamidoanisol.....	37	24	24	14	..	24
	..	24	24	14	..	24
Trinitroamidophenetol.....	37	24	24	14	..	24
	..	24	24	14	..	24
Trinitrometaphenylenediamine.....	33	24	24	14	..	24
	..	24	24	14	..	24
Trinitromethylnitraminoanisol.....	39	15	24	14	..	24
	..	16	24	14	..	24
Trinitromethylnitraminophenetol ...	34	19	24	14	..	24
	..	16	24	14	..	24

<sup>1</sup> At 23 and 24 cm. there was twice produced in 6 trials, a very incomplete explosion; the compounds simply inflamed.

### CONCLUSIONS

a. It has been shown repeatedly that Kast's apparatus and methods are satisfactory for obtaining precise results.<sup>2</sup>

b. The introduction of a methylnitramino or a fourth nitro group notably augments the sensibility, while an amino group lowers it; one may compare in this regard the following compounds:

Trinitrophenylmethylnitramine and trinitrodimethyldinitraminobenzene.

Trinitrophenol and trinitromethylnitraminophenol.

Trinitroaniline and aminotrinitrophenylmethylnitramine.

<sup>1</sup> In the table these heights are indicated briefly as follows: Maximum height from 0 to 6. Minimum height from 6 to 6.

<sup>2</sup> See also the detailed researches of Kast, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, 6, 7, 21, 67 (1911). On the subjects of the picrates and cresylates and trinitro bodies, it is not entirely clear why Kast tested these compounds with different heights of fall when he had previously recommended their determination by "maximum height from 0 to 6 and minimum height from 6 to 6." *Ibid.*, 4, 263 (1909). We have not encountered a similar condition elsewhere.

Trinitroaniline and tetranitroaniline.

Trinitrophenol and tetranitrophenol.

Trinitrophenylmethylnitramine and tetranitrophenylmethylnitramine.

Trinitrophenol and trinitroamidophenol.

Tetranitroaniline and the other tetranitro compounds.

It would be expected, *a priori*, that the alkylation of a phenol would diminish its sensitiveness; a comparison of trinitromethylnitraminophenol with the trinitromethylnitraminoanisol and phenetol shows clearly that this influence is great.

In addition to the nature of the group, the mobility thus introduced into richly substituted nitro compounds has also its influence;<sup>1</sup> the mobility increases the sensitiveness. This is why the aminonitrophenylmethylnitramine is more sensitive than tetryl; the amino group of the first diminishes its sensitiveness. Moreover, the methylnitramino group is much more mobile than in the tetryl and as a consequence it is possible to replace it by *m*-nitroaniline in the first body, while such is not the case for tetryl.<sup>2</sup>

*c.* The samples of dipicrylamine and 2,4,6,2',3',4'-hexanitrodiphenylamine show that the replacement of a fixed nitro group by a mobile nitro group produces a remarkable effect upon the sensitiveness.<sup>3</sup> In the 2,4,6,2',3',4'-hexanitrodiphenylamine the nitro group in the 3 position is very mobile, as shown by its direct reaction with dimethylaniline.

*d.* The data found in the literature on the subject of certain explosives are not exact. It is thus that Flürscheim<sup>4</sup> in the following table shows that tetranitroaniline is manifestly less sensitive than tetryl:

Weight of plunger, 5 kg.

	FIRST SERIES	SECOND SERIES	THIRD SERIES
Tetryl.....	25 cm.	50 cm.	35 cm.
Tetranitroaniline.....	45 cm.	60 cm.	50 cm.
Picric acid.....		35 cm.	

<sup>1</sup> Van Duin, *Rec. trav. chim.*, **38**, 89 (1919).

<sup>2</sup> Van Duin, *loc. cit.*

<sup>3</sup> See Will, *Ber. d. deutsch. chem. Ges.*, **47**, 704 (1914).

<sup>4</sup> Flürscheim, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **8**, 186 (1913). On this subject he has given an unacceptable explanation of these discordant values especially, but little confidence can be placed in the tests of the plunger and the difference in the quality of the nitro compounds. We believe that he worked each time with different and impure material.



Such series, for which it is evident that proper precautions have not been taken, cannot lead to any conclusion. The author shows, however, that the sensitiveness of tetryl and of tetranitroaniline for mercury fulminate is the same and this agrees with our results.<sup>1</sup>

Also it was shown that 2,4,6,3',4',6'-hexanitrodiphenylether is quite insensitive;<sup>2</sup> in fact the sensitiveness of this compound is greater than that of tetryl.

*e.* Certain of the explosives studied, the tetranitrophenylmethyl-nitramine and the trinitrodimethyldinitraminobenzene ought not to be included in the class of nitro explosives.

In 1906, Will<sup>3</sup> classified explosives according to their sensitiveness to a falling weight of 2 kg. as follows, and this classification is still of value:<sup>4</sup>

1st class.—Height of plunger 0 — 7 cm. To this class belong mercury fulminate, nitroglycerine, some picrates, etc.

2d class.—Height of plunger 7 — 25 cm. Includes among others the dynamites.

3d class.—Height of plunger 26 — 100 cm. Includes among others most of the aromatic nitro compounds.

4th class.—Height of plunger 100 — 200 cm. Includes many quite insensitive nitro compounds.

As we have demonstrated, sensitiveness increases by progressive substitution of nitro and methylnitramino groups in the benzene nucleus, and compounds formed by such substitutions belong to another class than that of the ordinary nitro explosives.

Finally, on the subject of the use of modern brisant explosives our previous publications should be consulted.<sup>5</sup>

HEMBRUG, ZAANDAM  
LABORATOIRE DE CHIMIE DE LA FABRIQUE DE MUNITIONS,  
March, 1919.

<sup>1</sup> See Bichel, *Glückauf*, **47**, 1194 (1905).

<sup>2</sup> Escales, "Nitrosprengstoffe," 82.

<sup>3</sup> Will, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **1**, 209 (1906).

<sup>4</sup> See Marshall, "Explosives, etc.," 1915, 345.

<sup>5</sup> Van Duin and Brackmann, *Chem. Weekl.*, **16**, 501 (1919).

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